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I. The Claisen Ester Condensation with Ethyl Thiolacetate

II. The Action of Sulphur on *n*-Heptane and *n*-Butane

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

RALPH BAYLIES BAKER

Baltimore, 1928

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PART I. THE CLAISEN ESTER CONDENSATION WITH ETHYL THIOLACETATE

Introduction

This investigation was undertaken with the idea in mind of comparing ethyl thiolacetate with ethyl acetate in the ordinary Claisen condensation. No sulfur esters have ever been subjected to such a reaction, and it appeared of interest to compare the products obtained with those resulting from the condensation of ethyl acetate with itself, and of ethyl acetate with a ketone and a nitrile.

Ethyl thiolacetate, $CH_3COSC_2H_5$, in the presence of sodium metal condenses in a manner quite similar to ethyl acetate, and forms a sulfur analog of acetoacetic ester, $CH_3COCH_2COSC_2H_5$. The yield of ester is rather low, being about 15% of the theoretical (calculated on the amount of ethyl thiolacetate used).

At ordinary temperatures ethyl acetothiolacetate contains about 31% of enol (determined by the bromo-titration method of Kurt Meyer),[1] as compared to about 7% in acetoacetic ester.

Acetothiolacetic ester forms metallic salts as does acetoacetic ester,[2] but the copper salt is the only one found that is stable. The others that were prepared decompose on short standing with the formation of metallic sulfides.

The conditions of hydrolysis of this ester are the same as those for acetoacetic ester. With dilute alkalies acetone is formed, and in the presence of concentrated alkalies, two molecules of acetic acid are liberated.

Like acetoacetic ester[3] the new ester decomposes on heating, but much more readily, with the formation of dehydracetic acid, $C_8H_8O_4$.

[1] Kurt Meyer, *Ber.*, **44**, 2718 (1911).

[2] Conrad, *Ann.*, **188**, 269 (1877); Wislicenus, *Ber.*, **31**, 3153 (1898); Lippmann, *Z. für Chemie*, **12**, 29 (1869).

[3] See Geuther, *Z. für Chemie*, 8 (1866).

An equal molar mixture of ethyl thiolacetate and ethyl acetate condenses in the presence of sodium, and a liquid is obtained having a composition of 98% of acetothiolacetic ester (by analysis for sulfur) and 2% of acetoacetic ester. This would show that ethyl thiolacetate is more reactive than ethyl acetate in this condensation.

The Claisen condensation also takes place between an ester and a ketone. Ehrhardt and Claisen[4] prepared acetylacetone, $CH_3COCH_2COCH_3$, by condensing ethyl acetate with acetone. In attempting the same reaction with ethyl thiolacetate and acetone, however, no acetylacetone is formed but only acetothiolacetic ester. The acetone apparently has no effect upon the ethyl thiolacetate, which merely condenses with itself.

Ethyl thiolacetate condenses with acetonitrile with the formation of cyanacetone, CH_3COCH_2CN, the yield amounting to 7%. This same compound is obtained from ethyl acetate and acetonitrile with the same yield.

Experimental

Ethyl Thiolacetate.—This ester was prepared by a modification of the method of Michler.[5] The calculated amount of acetyl chloride was added slowly from a dropping funnel through a reflux condenser to slightly more than the calculated amount of ethyl mercaptan, contained in a flask packed in ice. After the addition of the acetyl chloride, the dropping funnel was replaced by a piece of glass tubing leading to a flask containing water to absorb the hydrogen chloride and recover any mercaptan carried over. The mixture was kept at room temperature for several days and then heated under reflux. The product was poured into water. The upper layer was separated and was washed free of acids and dried over calcium chloride. It was then subjected to fractional distillation and the portion boiling at 116–117° collected; yield, 80% of theoretical. The following physical properties were obtained: $d_{4^\circ}^{0^\circ} = 1.0008$; $d_{4^\circ}^{25^\circ} = 0.9755$; $n_D^{28^\circ} = 1.4503$; mol. refr. $[(n^2-1)/(n^2+2)]M/d = 19.31$. Michler gives the boiling point as 114–116°. There are no data on the other properties in the literature.

Ethyl Acetothiolacetate, $CH_3COCH_2COSC_2H_5$

Preparation.—To 17 g. of sodium wire contained in a large balloon flask, 200 g. of ethyl thiolacetate was added slowly, in portions, through a reflux condenser. The top of the flask was packed with ice, as in a Grignard reaction, while the bottom was heated gradually on the water-bath to 50°. After six hours the sodium had all reacted and a yellowish pasty mass was obtained. After cooling, 50% acetic acid was added to an acid reaction. An equal volume of cold saturated sodium chloride solution was then added, the top layer separated and dried over calcium chloride. The liquid was fractionated at 2 mm. pressure in apparatus similar to that of Martin[6] as modified by Rice and Sullivan.[7] The distillate going over up to 60° bath temperature was discarded. At 60° and 2 mm. 22 g. (15% yield) of ethyl acetothiolacetate was collected. Sulfur was determined by the Parr bomb method, the liquid being introduced in small, thin-walled bulbs.

Anal. Calcd. for $C_6H_{10}O_2S$: S, 21.93. Found: S, 22.04, 21.86, 22.08.

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[4] Ehrhardt and Claisen, *Ber.*, **22**, 1011 (1889).

[5] Michler, *Ann.*, **176**, 182 (1875).

[6] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

[7] Rice and Sullivan, *J. Am. Chem. Soc.*, **50**, 3048 (1928).

Properties.—Ethyl acetothiolacetate is a colorless liquid with a rather disagreeable odor, having the following physical properties: $d_4^{0°} = 1.0917$; $d_4^{25°} = 1.0684$; $n_D^{25°} = 1.4885$; mol. refr. $[(n^2-1)/(n^2+2)]M/d = 39.46$. It is insoluble in water but dissolves in ether and alcohol in all proportions. It gives a deep red color with ferric chloride solution (presence of enol form) as does acetoacetic ester. It forms a white crystalline compound with sodium bisulfite.

Percentage of Enol Form.—A determination of the enol content of the ester by Kurt Meyer's bromo-titration method gave a mean value of 30.8%.

Metallic Salts: Copper Salt.—This salt was prepared by adding the calculated amount of a 6% solution of copper acetate to the ester diluted with 2 parts of ether. The bright green precipitate was filtered off, washed with water, then with alcohol and dried in a vacuum desiccator over sulfuric acid. The very fine crystals were found to be insoluble in water and only fairly soluble in benzene, alcohol, ether, chloroform and carbon tetrachloride, both in the hot and in the cold. The crystals decompose on heating at 110°. Copper was determined by the potassium iodide method after decomposing the organic salt in concentrated sulfuric and nitric acids. Sulfur was determined by the Parr bomb method.

Anal. Calcd. for $Cu(C_6H_9O_2S)_2$: Cu, 17.97; S, 18.12. Found: Cu, 18.12, 18.09; S, 18.01, 18.10.

Hydrolysis of Acetothiolacetic Ester

Ketone Hydrolysis.—Acetone is formed from the ester by refluxing with dilute alkali. For this purpose, 1 g. of the ester and 10 cc. of a 5% sodium hydroxide solution were refluxed for two hours in a boiling water-bath. Some of the liquid was then distilled off and acetone identified in the distillate by Gunning's method,[8] which is a modification of Lieben's iodoform test for acetone applicable in the presence of alcohol. A considerable amount of iodoform was obtained.

Acid Hydrolysis.—Acetic acid is obtained by refluxing the ester with concentrated alkali. To a solution of 3.5 g. of potassium hydroxide in 3 cc. of water, 2 g. of the ester was added. After heating in the boiling water-bath for several hours the liquid was acidified with sulfuric acid. The clear liquid was poured off from some potassium sulfate and distilled. Acetic acid was detected by the addition of absolute alcohol followed by concentrated sulfuric acid.

Decomposition of Ethyl Acetothiolacetate.—The residue from a vacuum distillation of the ester solidified on cooling. This solid was found to be very soluble in hot alcohol but insoluble in cold. After several crystallizations from alcohol, pale straw-colored needles were obtained, having a melting point of 109°. They were identified by melting point and molecular weight determinations as dehydracetic acid, $C_8H_8O_4$, a compound described by Geuther.[3]

Ethyl Thiolacetate and Ethyl Acetate.—A mixture of 50 g. of ethyl acetate and 59 g. of ethyl thiolacetate was added to 10 g. of sodium wire. After the metal had reacted, the product was worked up as above. The fraction coming over from 40–60° at 2 mm. (the boiling points of acetoacetic ester and acetothiolacetic ester, respectively) was collected. A Parr bomb analysis for sulfur gave 21.49%. As the theoretical value is 21.93%, this indicates 98% of ethyl acetothiolacetate. As a further check on this figure, the density of this liquid was taken at 25° and the value $d_4^{25} = 1.0657$ obtained.

From density measurements (at 25°) of a series of mixtures of the two esters (of known composition) a curve is obtained by plotting density against composition. The value of $d_4^{25} = 1.0657$ corresponds to a composition of 95% $CH_3COCH_2COSC_2H_5$, which agrees fairly well with the composition obtained by actual analysis.

[8] Gunning, *Z. anal. Chem.*, **24**, 147 (1885).

Ethyl Thiolacetate and Acetone.—The method of Ehrhardt and Claisen[4] for the preparation of acetylacetone from ethyl acetate and acetone was used with the sulfur ester in the hope of forming the same compound but only ethyl acetothiolacetate was obtained. Apparently the acetone does not take part in the reaction, and the sulfur ester simply condenses with itself.

Ethyl Thiolacetate and Acetonitrile.—A cold mixture of 38 g. of the ester and 14 g. of acetonitrile was added to 5 g. of sodium wire. After the reaction was complete, the solid was put carefully into ice water, the lower alkaline layer separated and acidified with dilute hydrochloric acid. This was extracted several times with ether, the extract separated, and dried over calcium chloride. The ether was distilled off, and the residue fractionated. The portion boiling from 120–125° was collected. The yield of cyanacetone was 7% of the acetonitrile used.

Summary

1. Ethyl thiolacetate condenses in the presence of sodium to form a sulfur analog of acetoacetic ester, $CH_3COCH_2COSC_2H_5$.

2. The mean value of the enol content of the sulfur ester, as determined by the bromo-titration method, is 30.8% at ordinary temperatures.

3. Acetothiolacetic ester forms metallic salts as does acetoacetic ester, but of those made only the copper salt, $C_{12}H_{18}O_4S_2Cu$, is stable.

4. Ethyl acetothiolacetate shows the ketone and acid hydrolysis, as does ethyl acetoacetate.

5. Upon heating, ethyl acetothiolacetate decomposes to form dehydracetic acid, $C_8H_8O_4$ as does ethyl acetoacetate.

6. An equal molar mixture of ethyl thiolacetate and ethyl acetate condenses with sodium to form 98% acetothiolacetic ester and 2% acetoacetic ester.

7. Ethyl thiolacetate and acetone do not condense with sodium to form acetylacetone as would be expected; ethyl acetothiolacetate alone is produced.

8. Ethyl thiolacetate and acetonitrile condense with sodium to form cyanacetone.

PART II. THE ACTION OF SULFUR ON NORMAL-HEPTANE AND NORMAL-BUTANE

Introduction

The action of sulfur on organic compounds has been the subject of many investigations.[1] Friedmann[2] investigated the action of sulfur on *n*-octane when heated under pressure. He obtained a thiophene, $C_8H_{12}S$, and a thiophthene compound, $C_8H_8S_2$.

The Present Investigation

n-Heptane and *n*-butane were heated with sulfur. The results obtained, so far as they go, are analogous to those of Friedmann. Heptane gives a substituted thiophene and *n*-butane seems to give thiophene itself, though the yields from both hydrocarbons were very small.

Experimental

***n*-Heptane. Sealed Pyrex Tubes.**—Three g. of sulfur and 11 g. of heptane were heated in each tube at temperatures varying from 150 to 250° for periods of four to twenty-four hours. On cooling the tubes were placed in "dry ice" before opening. The liquid was fractionated and consisted mostly of unchanged heptane. A very small residue boiling above 100° was obtained.

Steel Bombs.—Much larger amounts of materials were used in the bombs, which were heated to temperatures of 300–350° for periods of twenty-four to forty-eight hours. A charge consisted of 12.8 g. of sulfur and 40 g. of heptane. The residues from the bombs, after distilling off the unchanged heptane, were not much greater in proportion than those obtained from the glass tubes. There is very little indication of reaction under these conditions. However, the various residues were combined and fractionated. A fraction (about 2 g.) boiling at 160–161° was collected. A few drops of this liquid when treated with alcoholic mercuric chloride gave a pale yellow precipitate (test for thiophenes). Reasoning from the results of Friedmann's work on *n*-octane, heptane should give a thiophene of the empirical formula $C_7H_{10}S$. A

[1] See, for example, Steinkopf and Kirchoff, British patent 16,810, July 18, 1912; Capelle, *Bull. soc. chim.*, [4] **3**, 150 (1908); W. Friedmann, *Ber.*, **49**, 1551 (1916).

[2] Friedmann, *Ber.*, **49**, 1344 (1916).

Parr bomb determination of sulfur gave the result: calcd. for $C_7H_{10}S$: S, 25.40; found: S, 24.89, 25.04. The density was $d_{4^\circ}^{0^\circ} = 0.9332$; $d_{4^\circ}^{25^\circ} = 0.9221$.

This liquid gave positive tests for thiophenes by the methods of Fletcher and Hopkins,[3] Bauer[4] (indophenin reaction), Laubenheimer[5] and Steensma.[6] Negative tests were obtained when the liquid was examined for mercaptans[7] and sulfides.[8]

Considerable solid matter was left in the tubes after the removal of the liquid. This proved to be sulfur mixed with some carbon.

n-**Butane.**—Steel bombs were used with butane and sulfur, the charge being 32 g. of butane and 15 g. of sulfur. As butane is a gas at ordinary temperatures the bomb was first well cooled in an ice-salt mixture before adding the hydrocarbon. The charge was heated for twenty-one hours at 335°.

On opening the bomb (after again cooling in ice water), a considerable amount of hydrogen sulfide was given off and the unreacted butane was volatilized. The gas evolved smelled like a low-boiling gasoline high in sulfur content. Upon opening the bomb very little residue was left (less than 1 g.). This was taken up in ether, and gave all of the above-mentioned color tests for thiophene.

Conclusions

The results obtained are analogous to those obtained by Friedmann on octane. From heptane and sulfur a thiophene of the formula $C_7H_{10}S$ is formed in small amounts.

Similar results were obtained with butane and sulfur.

[3] Fletcher and Hopkins, *Chem. Zentr.*, I, 1442 (1907).
[4] Bauer, *Ber.*, **37**, 1244, 3128 (1904).
[5] Laubenheimer, *ibid.*, **8**, 224 (1875).
[6] Steensma, *Chem. Zentr.*, I, 1492 (1908).
[7] Reid, Mackall and Miller, *J. Am. Chem. Soc.*, **43**, 2104 (1921).
[8] Steinkopf, *Ann.*, **403**, 1 (1914).

BIOGRAPHY

The author of this dissertation, Ralph Baylies Baker, was born December 16, 1902, at Baltimore, Maryland. His early education was received at the Friends School in Baltimore. After graduating from that institution in 1921, he entered the Johns Hopkins University, where he received the degree of B.S. in Chemistry in June, 1925. In the fall of the same year he began the graduate study of chemistry at the Johns Hopkins University, and has been in attendance continuously since that time.